

What is claimed is:

1. A method for making a negative-working lithographic master for wet offset lithographic printing of an image on a printing medium,
5 comprising the steps of:
 - (a) coating a layer of positive-working radiation-imageable medium onto a hydrophilic lithographic base;
 - 10 (b) forming a mask on the surface of said radiation-imageable medium, said mask being in the form of said image and substantially resistant to a developer; and
 - (c) exposing said layer of radiation-imageable medium to said
15 developer to remove the areas of said radiation-imageable medium that are not covered by said mask.
2. A method for making a negative-working lithographic master, said method comprising the step of imaging a positive-working radiation-
20 imageable medium on a hydrophilic lithographic base.
3. A method for making a negative-working lithographic master for wet offset lithographic printing of an image on a printing medium,
25 comprising the steps of:
 - (a) providing a lithographic precursor comprising a layer of positive-working radiation-imageable medium coated on a hydrophilic lithographic base;

- (b) forming a mask on the surface of said radiation-imageable medium, said mask being in the form of said image and substantially resistant to a developer; and
- 5 (c) exposing said layer of radiation-imageable medium to said developer to remove the areas of said medium that are not covered by said mask.
- 10 4. A method for making a negative-working lithographic master from a positive-working radiation-imageable medium, comprising the step of imagewise depositing droplets of a masking fluid onto a layer of positive-working radiation-imageable medium on a hydrophilic lithographic base.
- 15 5. A method of performing wet offset printing of an image on a printing medium, comprising the steps of:
- 20 (a) providing an offset lithographic precursor comprising a layer of positive-working radiation-imageable medium on a hydrophilic lithographic base;
- (b) forming a mask upon the surface of said radiation-imageable medium, said mask being in the form of said image and substantially resistant to a developer;
- 25 (c) forming a lithographic master by exposing said layer of radiation-imageable medium to said developer to remove the areas of said developer that are not covered by said mask; and

(d) performing wet offset lithographic printing with said lithographic master.

5

6. A method for wet offset printing, said method comprising the steps of:

(a) making a negative-working lithographic master from a positive-working radiation-imageable medium; and

10

(b) performing wet offset lithographic printing with said lithographic master.

15

7. A negative-working lithographic master produced in accordance with the method of claim 1.

8. A lithographic master in accordance with claim 6 wherein said base is one of:

20

(a) a disposable plate;

(b) a re-usable plate;

(c) a printing cylinder of a printing press; and

25

(d) a seamless sleeve for a printing cylinder of a printing press.

30

9. A negative-working wet lithographic master comprising areas of hydrophobic positive-working radiation-imageable medium on a hydrophilic lithographic base.

10. A masked lithographic printing precursor for use in the wet offset printing of an image, comprising:
- 5
- (a) a hydrophilic lithographic base;
- (b) a layer of positive-working radiation-imageable medium coated on said base; and
- 10
- (c) a mask formed upon the surface of said layer of radiation-imageable medium, said mask being in the form of said image and substantially resistant to a developer.
11. A method according to claim 1 wherein said step of forming a mask comprises depositing droplets of a masking fluid.
- 15
12. A method according to claim 11 wherein said depositing is done by means of an inkjet printer.
13. A method according to claim 1 wherein said step of forming a mask includes the steps of curing said mask.
- 20
14. A method according to claim 13 wherein said curing is done by heating.
- 25
15. A method according to claim 14 wherein said heating is done at a temperature in the range of 40 - 130° C for a time in the range of 10 seconds to 3 minutes.

16. A method according to claim 1 further comprising the step of hardening the part of said layer of medium that remains on said base.
- 5 17. A method according to claim 1 further comprising, after step (c), the step of removing said mask.
18. A method according to claim 11 wherein said masking fluid comprises an indicator dye.
- 10 19. A method according to claim 11 wherein said masking fluid comprises an active masking ingredient and a solvent.
20. A method according to claim 19 wherein said solvent comprises water.
- 15 21. A method according to claim 19 wherein said solvent comprises an organic solvent.
22. A method according to claim 19 wherein said solvent comprises water and an organic solvent.
- 20 23. A method according to claim 9 wherein said masking fluid comprises a nitrogen-containing compound wherein at least one nitrogen atom is:
- 25 (a) quarternized; or
- (b) incorporated in a heterocyclic ring; or
- 30

(c) both quarternized and incorporated in a heterocyclic ring.

24. A method according to claim 23 wherein said nitrogen-containing compound is one of sub-paragraph:

5

(a) a triaryl methane dye, and

(b) a tetraalkyl ammonium compound.

- 10 25. A method according to claim 23 wherein said nitrogen-containing compound is one of:

(a) a quinoline;

15

(b) a triazole;

(c) an imidazole; and

(d) an indole.

20

26. A method according to claim 25 wherein said nitrogen-containing compound is 1,2,4-triazole.

27. A method according to claim 24 wherein said nitrogen-containing compound is one of:

25

(a) Crystal Violet;

(b) Ethel Violet; and

30

(c) Basic Blue 7.

28. A method according to claim 24 wherein said nitrogen-containing compound is one of:

5

(a) cetrimide; and

(b) a benzotrimethyl ammonium salt.

10 29. A method according to claim 23 wherein said nitrogen-containing compound is a quinolinium compound.

30. A method according to claim 29 wherein said quinolinium compound is one of:

15

(a) 1-ethyl-2-methyl quinolinium iodide; and

(b) 1-ethyl-4-methyl quinolinium iodide.

20 31. A method according to claim 23 wherein said nitrogen-containing compound is a benzothiazolylidene compound.

32. A method according to claim 31 wherein said benzothiazolydene compound is 3-ethyl-2-methyl benzothiazolium iodide.

25

33. A method according to claim 23 wherein said nitrogen-containing compound is a pyridinium compound.

34. A method according to claim 33 wherein said pyridinium compound is one of:

30

(a) cetyl pyridinium bromide;

(b) ethyl viologen dibromide; and

5 (c) fluoropyridinium tetrafluoroborate.

35. A method according to claim 29 wherein said quinolinium compound is a cationic cyanine dye.

10 36. A method according to claim 35 wherein said dye is one of:

(a) Dye A; and

(b) Quinoldine Blue.

15

37. A method according to claim 31 wherein said benzothiazolium compound is 3-ethyl-2-[3-ethyl-2(3H)-benzothiazoylidene)-2-methyl-1-propenyl] benzothiazolium iodide.

20 38. A method according to claim 11 wherein said masking fluid comprises one of:

(a) a flavone;

25 (b) a flavonone;

(c) an isoflavanone;

(d) a coumarin;

30

- (e) a chromone;
- (f) an indeneone;
- 5 (g) a chalcone;
- (h) a xanthone;
- (i) a thioxanthone;
- 10 (j) benzophenone;
- (k) a phthalimide; and
- 15 (l) a phenanthrenequinone.

39. A method according to claim 38 wherein said flavone is one of:

- (a) 7,8-benzoflavone;
- 20 (b) trihydroxyflavone; and
- (c) naphthaflavone.

25 40. A method according to claim 38 wherein said flavanone is hydroxy-dimethoxyflavanone.

41. A method according to claim 11 wherein said masking fluid
comprises a poly substituted siloxane.

30

42. A method according to claim 41 wherein said siloxane is polyphenylsiloxane.
- 5 43. A method according to claim 11 wherein said masking fluid comprises a substituted pyran.
44. A method according to claim 11 wherein said making fluid comprises a perfluorinated compound.
- 10 45. A method according to claim 11 wherein said masking fluid comprises acridine orange base.
46. A method according to claim 19 wherein the amount of said active masking ingredient is in the range of 0.5 - 5 weight % of said masking fluid.
- 15 47. A method according to claim 11 wherein said masking fluid further comprises one or more of:
- 20 (a) a humidifying co-solvent;
- (b) a dye;
- (c) a surfactant or wetting agent; and
- 25 (d) a biocide.
48. A method according to claim 1 wherein said radiation-imageable medium is a quinonediazide.
- 30

49. A method according to claim 48 wherein said quinonediazide is a 1,2-naphthoquinone-2-diazide-4- or -5- sulfonyl derivative.
50. A method according to claim 48 wherein said quinonediazide is a naphthoquinonediazide.
51. A method according to claim 50 wherein the amount of said naphthoquinonediazide is in the range of 3 - 50 weight % relative to the weight of non-volatile components of said radiation-imageable medium.
52. A method according to claim 1 wherein said radiation-imageable medium comprises a binder.
53. A method according to claim 52 wherein said binder is a novolak polycondensate.
54. A method according to claim 52 wherein said binder is a polyhydroxyphenyl resin.
55. A method according to claim 52 wherein said binder is a polymer or co-polymer of an acrylic or methacrylic acid ester with a polyhydricphenol.
56. A method according to claim 52 wherein the amount of said binder is in the range of 30 - 90 % by weight relative to total solids in said medium.

57. A method according to claim 52 wherein the amount of said binder is in the range of 50 - 85 % by weight relative to total solids in said medium.
- 5 58. A method according to claim 52 wherein said binder has phenolic hydroxyl groups present in the range of about 1 - 15 mmol/g and a molecular weight up to 100,000.
- 10 59. A method according to claim 52 wherein said binder comprises a combination of a cresol/formaldehyde novolak and an unplasticized, alkyl-etherified melamine/formaldehyde resin.
60. A method according to claim 1 wherein said radiation-imageable medium comprises or more of:
- 15 (a) a polyglycol;
- (b) a cellulose derivative;
- 20 (c) a dye;
- (d) an adhesion promoter;
- (e) a pigment; and
- 25 (f) a UV-absorber.
61. A method according to claim 1 wherein said step of coating comprises dissolving said radiation-imageable medium in a solvent and applying it by one of:
- 30

(a) spraying;

(b) dipping;

5 (c) roller application;

(d) slot dies;

10 (e) blade application; and

(f) coater application.

62. A method according to claim 1 wherein said lithographic base is
15 anodized aluminum.

63. A method according to claim 1 wherein said developer is an
aqueous alkaline solution.

64. A method according to claim 63 wherein said solution has a pH in
20 the range of 10-14.

65. A method according to claim 63 wherein said solution further
includes one or more of:

25 (a) an organic solvent;

(b) a surfactant; and

30 (c) a sequestering agent.

- 5 66. A method according to claim 1, further including the step, after step (b), of flood-illuminating said layer of radiation-imageable medium with ultra-violet radiation, and wherein said developer is a developer of the type capable of removing the areas of said radiation-imageable medium that are not covered by said mask after said radiation-imageable medium has been illuminated with ultra-violet radiation.
- 10 67. A method according to claim 66 wherein said developer comprises a quaternary nitrogen compound.
68. A method according to claim 67 wherein said developer comprises tetramethylammonium hydroxide in water.
- 15 69. A masking fluid for forming a mask on the surface of a layer of positive-working radiation-imageable medium, comprising:
- (a) an active masking ingredient that is substantially resistant to a developer; and
- 20 (b) a solvent capable of dissolving said active masking ingredient and of not substantially removing said positive-working radiation-imageable medium from a hydrophilic lithographic base.
- 25